

corr. EP 0313 146 A2

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

**0 313 146
A2**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **88202253.6**

(51) Int. Cl.4: **C11D 3/12 , C11D 3/20**

(22) Date of filing: **10.10.88**

(30) Priority: **19.10.87 GB 8724463**
24.03.88 GB 8807013

(43) Date of publication of application:
26.04.89 Bulletin 89/17

(84) Designated Contracting States:
AT BE CH DE FR GB GR IT LI LU NL SE

(71) Applicant: **THE PROCTER & GAMBLE
COMPANY**
One Procter & Gamble Plaza
Cincinnati Ohio 45202(US)

(72) Inventor: **Busch, Alfred**
Luitberg 10
B-1820 Strombeek-Bever(BE)
Inventor: **Baeck, Andre**
Putsesteenweg 273
B-2820 Bonhelden(BE)
Inventor: **Dekker, Bob**
Kasteelstraat 53/II
B-1820 Strombeek-Bever(BE)

(74) Representative: **Canonici, Jean-Jacques et al**
Procter & Gamble European Technical
Center N.V. Temselaan 100
B-1820 Strombeek-Bever(BE)

(54) **Detergent compositions.**

(57) Detergent compositions are disclosed which comprise a fabric softening, smectite-type clay. The clay is treated with organic humectants to enhance the softening benefit.

EP 0 313 146 A2

DETERGENT COMPOSITIONS

The present invention relates to detergent compositions containing a fabric-softening amount of a smectite-type clay. The clay is present in the form of agglomerates which comprise from 0.5% to 30% of an organic humectant.

5 British Patent 1,572,815 discloses a detergent composition based on soap and a curd-dispersing agent. The compositions comprise from 4% to 25% of a smectite-type clay. The clay is agglomerated with water, an aqueous electrolyte solution, a nonionic surfactant, or an aqueous solution of an organic adhesive. Examples of such adhesives include dextrin, gelatine, carboxymethyl-cellulose, starch, carboxymethyl starch, and alkyl and hydroxy alkyl substituted celluloses and starches. The agglomerates are disclosed to
10 minimize dustiness while the full softening potential of the clay is preserved.

British Patent 1,167,037 discloses clays that have been treated with alkanolamine salts and an organic humectant. The treated clays are disclosed to hydrate rapidly and to develop viscosity in a short period of time as compared to untreated clays.

15 British Patent 1,400,898 discloses detergent compositions comprising, as a fabric softening ingredient, a smectite-type clay.

It is now well recognized in the detergent industry that clays of the type disclosed in British Patent 1,400,898 provide significant fabric softening benefits when used in a laundry detergent. Yet, it is equally well recognized that deposition of these clays onto the fabrics during the laundering process is far from complete; in fact, under typical European laundry conditions, less than half of the available clay is deposited
20 onto the fabrics, the remainder being rinsed away with the laundry liquor during the subsequent rinsing steps. Moreover, the softening effect obtained as a result of the clay deposition is affected by factors that are not well understood.

It is, therefore, an object of the present invention to pretreat fabric-softening clays so as to increase the softening benefit obtained.

25

Summary of the Invention

30 The present invention relates to the granular detergent compositions comprising a) conventional detergent ingredients; and b) clay agglomerates comprising from 60% to 99.5% smectite-type clay and from 30% to 0.5% of an organic humectant. Preferred humectants include:

- a) aliphatic hydro-carbon polyols having from 2 to 9 carbon atoms;
- b) ether alcohols derived from the polyols of a);
- 35 c) ester alcohols derived from the polyols of a);
- d) mono- and oligosaccharides; and mixtures thereof.

Highly preferred agglomerates further comprise, by weight of the clay, from 0.005% to 20% of a clay flocculating agent.

40 Preferred clay flocculating agents are polymers like poly(ethylene oxide), poly(acryl amide) and poly(acrylate), having a weight average molecular weight of from 100,000 to 10 million. Most preferred are poly(ethylene oxide) polymers having a molecular weight (weight average) in the range 150,000 to 5 million.

Detailed Description of the Invention

45

The detergent compositions of the present invention comprise conventional deterative surfactants, conventional detergent builders and, optionally, other conventional detergent ingredients. The compositions further comprise a fabric-softening amount, typically from 1% to 35% by weight preferably from 3% to 15%
50 by weight of the detergent composition, of the fabric-softening clay agglomerates herein.

Percentages herein are percentages by weight of the detergent compositions, unless otherwise specified.

Detergent Ingredients

Deterative Surfactants -

The compositions of this invention will typically contain organic surface-active agents ("surfactants") to provide the usual cleaning benefits associated with the use of such materials. Deterative surfactants useful herein include well-known synthetic anionic, nonionic, amphoteric and zwitterionic surfactants. Typical of these are the alkyl benzene sulfonates, alkyl- and alkylether sulfates, paraffin sulfonates, olefin sulfonates, alkoxyated (especially ethoxyated) alcohols and alkyl phenols, amine oxides, alpha-sulfonates of fatty acids and of fatty acid esters, and the like, which are well-known from the detergency art. In general, such deterative surfactants contain an alkyl group in the C₉-C₁₈ range; the anionic deterative surfactants can be used in the form of their sodium, potassium or triethanolammonium salts; the nonionics generally contain from about 5 to about 17 ethylene oxide groups. U.S. Patent 3 995 669, the disclosures of which are incorporated herein by reference, contains detailed listings of such typical deterative surfactants.

C₁₁-C₁₆ alkyl benzene sulfonates, C₁₂-C₁₈ paraffin-sulfonates and alkyl sulfates, and the ethoxyated alcohols and alkyl phenols are especially preferred in the compositions of the present type. Also useful herein as the surfactant are the water-soluble soaps, e.g. the common sodium and potassium coconut or tallow soaps well-known in the art.

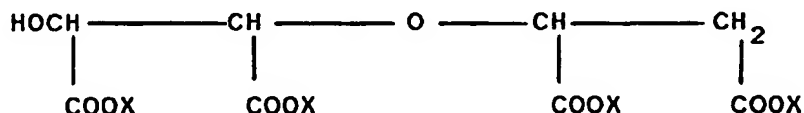
The surfactant component can comprise as little as 1% of the compositions herein, but preferably the compositions will contain 5% to 40%, preferably 10% to 30%, of surfactant. Mixtures of the ethoxyated nonionics with anionics such as the alkyl benzene sulfonates, alkyl sulfates and paraffin sulfonates are preferred for through-the-wash cleansing of a broad spectrum of soils and stains from fabrics.

Deterative Adjuncts -

The composition herein can contain other ingredients which aid in their cleaning performance. For example, it is highly preferred that through-the-wash detergent compositions contain a detergent builder and/or metal ion sequestrant. Compounds classifiable and well-known in the art as detergent builders include the nitrilotriacetates, polycarboxylates, citrates, carbonates, zeolites, water-soluble phosphates such as tri-polyphosphate and sodium ortho- and pyro-phosphates, silicates, and mixtures thereof. Metal ion sequestrants include all of the above, plus materials like ethylenediaminetetraacetate, the amino-polyphosphonates (DEQUEST) and a wide variety of other poly-functional organic acids and salts too numerous to mention in detail here. See U.S. Patent 3 579 454 for typical examples of the use of such materials in various cleaning compositions. In general, the builder/sequestrant will comprise about 0.5% to 45% of the composition. The 1-10 micron size zeolite (e. g. zeolite A) builders disclosed in German patent 2 422 655 are especially preferred for use in low-phosphate compositions.

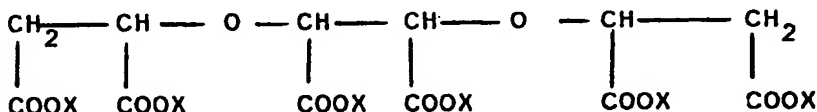
Particularly suitable phosphate-free builders are ether carboxylate mixtures comprising

a) from 1% to 99% of a tartrate monosuccinate component of the structure



wherein X is H or salt-forming cation; and

b) from 1% to 99% by weight of a tartrate disuccinate component of the structure :



wherein X is H or a salt-forming cation.

Builder systems of this type are more fully disclosed in U.S. patent N° 4,663,071, issued May 5, 1987

to Bush et al, the disclosures of which are incorporated herein by reference.

Typical detergent compositions contain from 5% to 35% of this builder system.

The laundry compositions herein also preferably contain enzymes to enhance their through-the-wash cleaning performance on a variety of soils and stains. Amylase and protease enzymes suitable for use in detergents are well-known in the art and in commercially available liquid and granular detergents. Commercial detergent enzymes (preferably a mixture of amylase and protease) are typically used at levels of 0.001% to 2%, and higher, in the present compositions. Detergent cellulase enzymes provide both cleaning and softening benefits, particularly to cotton fabrics. These enzymes are highly desirable in the detergent compositions of this invention.

The compositions herein can contain other ingredients which aid in their cleaning performance. For example, the compositions herein can advantageously contain a bleaching agent, especially a peroxyacid bleaching agent. In the context of the present invention, the term peroxyacid bleaching agent encompasses both peroxyacids per se and systems which are able to yield peroxyacids in situ.

Peroxyacids per se are meant to include the alkaline and alkaline-earth metal salts thereof. Peroxyacids and diperoxyacids are commonly used; examples are diperoxydodecanoic acid (DPDA) or peroxyphthalic acid.

Systems capable of delivering peracids in situ consist of a peroxygen bleaching agent and an activator thereof.

The peroxygen bleaching agents are those capable of yielding hydrogen peroxide in an aqueous solution; these compounds are well-known in the art, and include hydrogen peroxide, alkali-metal peroxides, organic peroxide bleaching agents such as urea peroxide, inorganic persalt bleaching agents such as alkali metal perborates, percarbonates, perphosphates, persulfates, and the like.

Preferred are sodium perborate, commercially available in the form of mono- and tetra-hydrates, sodium carbonate peroxyhydrate, sodium pyrophosphate peroxyhydrate and urea peroxyhydrate.

The liberated hydrogen peroxide reacts with a bleach activator to form the peroxyacid bleach. Classes of bleach activators include esters, imides, imidazoles, oximes, and carbonates. In these classes, preferred materials include methyl o-acetoxy benzoates; sodium-p-acetoxy benzene sulfonates such as sodium 4-nonanoxyloxybenzene sulfonate; sodium-4-octanoxyloxybenzene sulfonate, and sodium-4-decanoxyloxybenzenesulfonate; biophenol A diacetate; tetra acetyl ethylene diamine; tetra acetyl hexamethylene diamine; tetra acetyl methylene diamine.

Other highly preferred peroxygen bleach activators which are disclosed in U.S. Patents 4,483,778 and 4,539,130, the disclosures of which are incorporated herein by reference, are alpha-substituted alkyl or alkenyl esters, such as sodium-4(2-chlorooctanoxyloxy)benzene sulfonate, sodium 4-(3,5,5-trimethyl hexanoxyloxy)benzene sulfonate. Suitable peroxyacids are also peroxygen bleach activators such as described in published European Patent Application N° 0 116 571, i.e., compounds of the general type RXA⁺OOH and RXAL, wherein R is a hydroxycarbonyl group, X is a hetero-atom, A is a carbonyl bridging group and L is a leaving group, especially oxybenzenesulfonate.

Other highly desirable detergent ingredients for use in the detergent compositions of the present invention are quaternary ammonium compounds of the formula $R_4R_5R_6R_7N^+X^-$, wherein R_4 is alkyl having from 8 to 20, preferably from 12-18 carbon atoms, R_5 is alkyl having from 1 to 10 carbon atoms, and R_6 and R_7 are each C_1 to C_4 alkyl preferably methyl; X^- is an anion, e.g. chloride. Examples of such quaternary ammonium compounds include C_{12} - C_{14} alkyl trimethyl ammonium chloride and cocoalkyl trimethyl ammonium methosulfate. The quaternary ammonium compounds can be used at levels from 0.5% to 5%, preferably from 1% to 3%.

The fabric softening clay

Smectite-type clays are widely used as fabric softening ingredients in detergent compositions. Most of these clays have a cation exchange capacity of at least 50 meq/100g.

Montmorillonite clays are commonly used for this purpose. It appears, however, that certain hectorite clays provide better fabric softening performance than the more commonly used montmorillonites. The hectorites exhibiting this superior fabric softening performance are hectorites of natural origin having a lath-type shape.

According to the present invention, the fabric softening clay is present in the form of agglomerates. These agglomerates comprise, in addition to the clay, an organic humectant. The agglomerates optionally further comprise a polymeric clay flocculating agent. Typically, the agglomerates comprise by weight of the agglomerate, from 60% to 99.5% of the clay; from 0.5% to 30% of the humectant; and from 0% to 10% of

the clay flocculating agent. Preferably, the agglomerates further contain a heavy metal sequestering agent. Examples include heavy metal chelators, like EDTA and ethylenediamine tetramethylene phosphonic acid (EDTP). The agglomerates typically contain from 0.1% to 10% of the chelator.

5

The humectant

The organic humectant employed in the clay agglomerates may be any of the various water soluble materials utilized for such a purpose. The organic humectant is preferably selected from the group
 10 consisting of a) aliphatic hydrocarbon polyols having from 2 to 9 carbon atoms; b) ether alcohols derived from the polyols of a); c) ester alcohols derived from the polyols of a); d) mono- and oligosaccharides; and mixtures thereof.

Highly preferred humectants include glycerol, ethylene glycol, propylene glycol and the dimers and trimers of glycerol, of ethylene glycol and of propylene glycol.

15 The clay agglomerates comprise from 0.5% to 30%, preferably from 2% to 15%, of the humectant.

The optional clay flocculating agent

20 Clay-flocculating agents are not commonly used in detergent compositions. On the contrary, one is inclined to use clay dispersants, which aid in removing clay stains from fabrics. Flocculating agents are, however, very well known in other industries like oil well drilling, and for ore flotation in metallurgy. Most of these materials are fairly long chain polymers and copolymers derived from such monomers as ethylene oxide, acrylamide, acrylic acid, dimethylamino ethyl methacrylate, vinyl alcohol, vinyl pyrrolidone, ethylene
 25 imine. Gums, like guar gum, are suitable as well.

Preferred are polymers of ethylene oxide, acryl amide, or acrylic acid. It has been found that these polymers dramatically enhance the deposition of a fabric softening clay if their molecular weights (weight average) are in the range of from 100,000 to 10 million. Preferred are such polymers having a (weight average) molecular weight of from 150,000 to 5 million.

30 The most preferred polymer is poly (ethylene oxide). Molecular weight distributions can be readily determined using gel permeation chromatography, against standards of poly (ethylene oxide) of narrow molecular weight distributions.

The clay agglomerates herein comprise, by weight of the clay, from 0% to 20% clay flocculating agent, preferably from 0.05% to 20% by weight of the clay if the molecular weight is 150,000 - 800,000 and from
 35 0.005% to 2% by weight of the clay if its molecular weight is from 800,000 to 5 million.

Additional softening ingredients

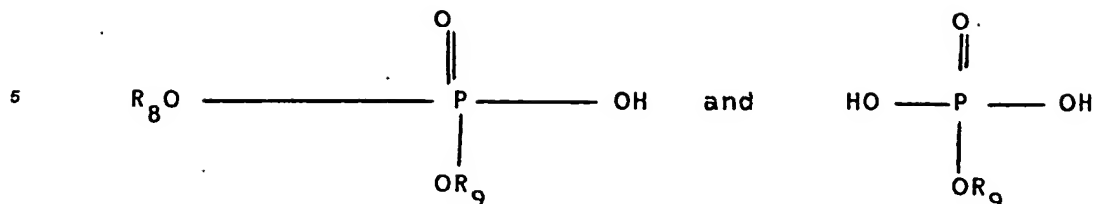
40

The detergent compositions of the present invention may further contain, in addition to the clay material, other softening ingredients. Suitable examples include amines of the formula $R_1R_2R_3N$, wherein R_1 is C_6 to C_{20} hydrocarbyl, R_2 is C_1 to C_{20} hydrocarbyl, and R_3 is C_1 to C_{10} hydrocarbyl or hydrogen. A preferred amine of this type is ditallowmethylamine.

45 Preferably, the softening amine is present as a complex with a fatty acid of the formula $RCOOH$, wherein R is a C_8 to C_{20} alkyl or alkenyl. It is desirable that the amine/fatty acid complex be present in the form of microfine particles, having a particle size in the range of from, e.g., 0.1 to 20 micrometers. These amine/fatty acid complexes are disclosed more fully in European Patent Application N° 0 133 804, the disclosures of which are incorporated herein by reference. Preferred are compositions that contain from 1%
 50 to 10% of the amine.

Suitable are also complexes of the above described amine and phosphate esters of the formula

65



wherein R_8 and R_9 are C_1 - C_{20} alkyl, or ethoxylated alkyl groups of the general formula $\text{alkyl}-(\text{OCH}_2\text{CH}_2)_y$, wherein the alkyl substituent is C_1 - C_{20} , preferably C_8 - C_{16} , and y is an integer of 1 to 15, preferably 2-10, most preferably 2-5. Amine/phosphate ester complexes of this type are more fully disclosed in European Patent Application N° 0 168 889, the disclosures of which are incorporated herein by reference.

Further examples of optional softening ingredients include the softening amides of the formula $\text{R}_{10}\text{R}_{11}\text{NCOR}_{12}$, wherein R_{10} and R_{11} are independently selected from C_1 - C_{22} alkyl, alkenyl, hydroxy alkyl, aryl, and alkyl-aryl groups; R_{12} is hydrogen, or a C_1 - C_{22} alkyl or alkenyl, an aryl or alkyl-aryl group. Preferred examples of these amides are ditallow acetamide and ditallow benzamide. Good results are obtained when the amides are present in the composition in the form of a composite with a fatty acid or with a phosphate ester, as described hereinbefore for the softening amines.

The amides are present in the composition at 1%-10% by weight.

Suitable softening ingredients are also the amines disclosed in U.K. Patent Application GB 2 173 827, the disclosures of which are incorporated herein by reference, in particular the substituted cyclic amines disclosed therein. Suitable are imidazolines of the general formula 1-(higher alkyl) amido (lower alkyl)-2-(higher alkyl)imidazoline wherein higher alkyl is alkyl having from 12 to 22 carbon atoms, and lower alkyl is alkyl having from 1 to 4 carbon atoms.

A preferred cyclic amine is 1-tallowamidoethyl-2-tallowimidazoline. Preferred compositions contain from 1% to 10% of the substituted cyclic amine.

The amine and amide softening ingredients may be added as a dry powder to a detergent granule, or may be sprayed onto the detergent granule or onto a carrier, either in melted or in dissolved form. An example of a suitable carrier is perborate monohydrate.

Moreover, the compositions herein can contain, in addition to ingredients already mentioned, various other optional ingredients typically used in commercial products to provide aesthetic or additional product performance benefits. Typical ingredients include pH regulants, perfumes, dyes, bleach, optical brighteners, soil suspending agents, hydrotropes and gel-control agents, freeze-thaw stabilizers, bactericides, preservatives, suds control agents, bleach activators and the like.

In a through-the-wash mode, the compositions are typically used at a concentration of at least 400 ppm, preferably 0.05% to 1.5%, in an aqueous laundry bath at pH 7-11 to launder fabrics. The laundering can be carried out over the range from 5° C to the boil, with excellent results.

Industrial Application

The agglomeration process itself may be performed using any of the techniques and apparatus which are conventional in the art (see e.g. "A review of Detergent Agglomeration" - M.J. DOLAN, HAPPI, April 1987 p 84-85). It can be batchwise or continuous. The optimum operating conditions (preferred granule size and moisture level) can be found by trial adjustments of process parameters such as the liquid spray-on level, rate and droplet size, the residence time, etc.

EXAMPLE 1

40 kg of a commercial smectite clay (CEC \geq 50 meq/100g.) were sprayed with 5 l. of a 40% by weight aqueous solution of glycerol in a Lödige drum agglomerator. After drying and sieving, the following agglomerate composition was obtained :

Smectite clay (anh.)	81.9%
Glycerol	4.1%
Moisture	14.0%

5

Granulometry : 212 μm (65 mesh) < min. 80% < 850 μm (20 mesh).

A reference agglomerate, i.e. no glycerol was made in the same way.

Both agglomerates were dry mixed with a spray-dried granular detergent to yield the following compositions:

10

	A	B
LAS	7	7
STPP	24	24
EDTA	0.2	0.2
Brightener	0.2	0.2
Sodium silicate	6.0	6.0
Suds suppressor	0.4	0.4
NA ₂ CO ₃	10.0	10.0
PB ₄ (*)	20.0	20.0
Proteolytic enzyme (*)	0.5	0.5
Na ₂ SO ₄ + H ₂ O	balance	
	93.5	93.5
Clay/ glycerol agglomerates	6.5	—
Clay Reference agglomerate	—	6.5
	100.0	100.0

25

(*) Dry mixed

30

The compositions A and B were then used to wash 4 Kg clean fabric loads in a MIELE washing machine. The water hardness was 3.0 mmol (Ca⁺⁺ + Mg⁺⁺)/l and the detergent concentration was 10 g/l. Clean terry towel tracers were added to permit evaluation of 1 cycle and cumulative (4 cycles) softening performance. Softness tracers were line dried prior to assessment by expert judges. A 0 → 4 panel score units (p.s.u.) scale was used for grading, in which 0 means no difference and 4 stands for a very big difference.

35

Composition A was rated better for softness than B :

40

1 cycle tracers	0.6 p.s.u. (s)
4 cycle tracers	0.8 p.s.u. (s)
(s) Differences are statistically significant at 95% confidence level.	

45

It can thus be seen that composition A, in accordance with the invention is superior in fabric softening performance to the prior art composition A.

The following agglomerate compositions are obtained, using the procedure outlined under Example I

50

55

	II	III	IV	V
Smectite clay (anh.)	79.5%	83.4%	81%	74%
Ethylene glycol	8.0%	2.1%	-	6%
Sorbitol	-	-	4%	-
Polyethylene oxide (1)	-	-	-	5 %
Moisture	12.5%	14.5%	15%	13 %
EDTP	-	-	-	2 %

(1) having weight average molecular weight of about 300.000.

The clay agglomerates may also be incorporated in a laundry additive, as such or with the aid of a water soluble and/or insoluble carrier such as e.g. a sheet or a pouch. These agglomerates, as such or with a suitable carrier, can then be added to the wash liquor on top of a conventional detergent composition. The laundry additive preferably also contains one or more of the additional softening ingredients specified before. The additive may thus be used in conjunction with detergent compositions that themselves do not contain such a clay and/or these other softening ingredients.

20 Claims

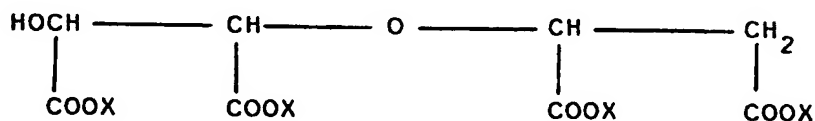
1. A granular detergent composition comprising
 - a) conventional detergent ingredients; and
 - b) clay agglomerates comprising from 70% to 99.5% smectite-type clay and from 30% to 0.5% of an organic humectant.
2. A detergent composition according to Claim 1, characterized in that the organic humectant is selected from
 - a) aliphatic hydrocarbon polyols having from 2 to 9 carbon atoms ;
 - b) ether alcohols derived from the polyols of a);
 - c) ester alcohols derived from the polyols of a);
 - d) mono- and oligosaccharides; and
 - e) mixtures thereof.
3. A detergent composition according to Claim 1 or 2, wherein the clay agglomerates comprise from 2% to 15% of the organic humectant.
4. A detergent composition according to any one of the preceding claims wherein the humectant is selected from glycerol, ethylene glycol, propylene glycol, the dimers and trimers of glycerol, ethylene glycol and propylene glycol, and mixtures thereof.
5. A detergent composition according to any one of the preceding claims characterized in that the clay agglomerates further comprise from 0.005% to 20% by weight of the clay of a polymeric clay flocculating agent.
6. A detergent composition according to claim 5, characterized in that the clay agglomerates further comprise from 0.1% to 10% of a chelator, preferably EDTA, EDTP, or mixtures thereof.
7. A detergent composition according to Claim 5 wherein the polymeric clay flocculating agent has a weight average molecular weight of from 150.000 to 5 million.
8. A detergent composition according to Claim 6 or 7 wherein the polymer is derived from monomers selected from ethylene oxide, acrylamide, and acrylic acid.
9. A detergent composition according to any one of the preceding claims, further comprising from 0.5% to 5% of a quaternary ammonium compound of the formula $R_4R_5R_6R_7N^+X^-$, wherein R_4 is alkyl having from 10 to 20 carbon atoms, R_5 , R_6 and R_7 are each C_1 to C_4 alkyl, and X^- is an anion.
10. A detergent composition according to any one of the preceding claims further comprising from 1% to 10% of an amide of the formula $R_{10}R_{11}NCOR_{12}$, wherein R_{10} and R_{11} are independently selected from C_1 - C_{22} alkyl, alkenyl, hydroxy alkyl, aryl, and alkyl-aryl groups; R_{12} is hydrogen, or a C_1 - C_{22} alkyl or alkenyl, aryl or alkyl-aryl group, or is $O-R_{13}$, wherein R_{13} is a C_1 - C_{22} alkyl or alkenyl, an aryl or alkyl-aryl group.

11. A detergent composition according to any one of the preceding claims further comprising from 1% to 10% of imidazolines of the formula 1-(R₁₄) amido (R₁₅)-2-(R₁₆) imidazoline where R₁₄, R₁₆ are independently selected from C₁₂-C₂₂ alkyl and R₁₅ from C₁-C₆ alkyl.

12. A detergent composition according to any one of the preceding claims comprising from 1% to 10% of amines of the formula R₁R₂R₃N wherein R₁ is C₆ to C₂₀ hydrocarbyl, R₂ is C₁ to C₂₀ hydrocarbyl; and R₃ is C₁ to C₁₀ hydrocarbyl or hydrogen.

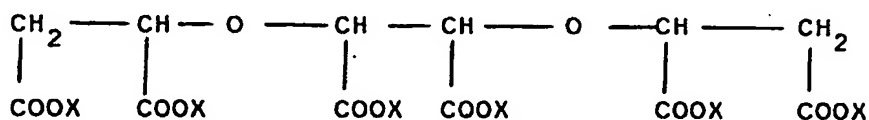
13. A detergent composition according to any one of the preceding claims, further comprising from 5% to 35% of a builder system, said builder system comprising

a) from 1% to 99% of a tartrate monosuccinate component of the structure :



wherein X is H or a salt-forming cation; and

b) from 1% to 99% by weight of a tartrate disuccinate component of the structure :



wherein X is H or a salt-forming cation.

14. A laundry additive containing a clay agglomerate comprising from 70% to 99.5% by weight smectite type clay and from 30% to 0.5% by weight of an organic humectant as defined in Claim 2.

15. The additive in accordance with Claim 14 wherein the organic humectant represents from 2% to 15% by weight.

16. The additive in accordance with Claims 14 and 15 which in addition comprises from 0.005% to 20% by weight of the clay of a polymeric clay flocculating agent.

17. The additive in accordance with claims 14-16 which in addition comprises an additional softening ingredient as defined in claims 8, 9 and 10 in an amount of from 2% to 50% by weight, preferably from 5% to 30% by weight.

18. The additive in accordance with claims 14-17 which is deposited onto/contained within a suitable water-soluble or water-insoluble carrier.